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The Combined Influence of Solution Resistance and  
Charge-Transfer Kinetics on Microelectrode Cyclic Voltammetry

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9 ABSTRACT (Continue on reverse if necessary and identify by block number) The effects of heterogeneous kinetics on cyclic voltammograms at microdisk electrodes are examined by digital simulation. The increased diffusive efficiency at microelectrodes raises the upper limit of measurable rate constant relative to a large electrode. Solution resistance, often considered to be insignificant at microelectrodes, is shown to have potentially serious influence on the shape of the voltammogram. When solution resistance and heterogeneous kinetics are combined, the results suggest complex coupling between the effects of these parameters, thus making their separation difficult. Key words:					
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Preliminary note

## The combined influences of solution resistance and charge-transfer kinetics on microelectrode cyclic voltammetry

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### INTRODUCTION

Since the introduction of electrodes with microscopically small dimensions several years ago, their advantages in interrogating fast heterogeneous and homogeneous kinetic systems have been publicized widely [1–4]. Their virtues are predicated in large part on the diminution of the effects of solution resistance brought about by decreasing the electrode size. However, surprisingly few attempts have been made to treat the inevitable remaining effects of solution resistance on the electrochemical response of microelectrodes in common situations [1,2,5–7].

The most popular experiments to date involve voltammetry using inlaid disk electrodes. For such measurements, there are three distinct regimes: high scan rates where radial (i.e. non-linear) diffusion is insignificant, low scan rates where a steady-state condition is established, and intermediate scan rates where no steady state is achieved, but radial diffusion cannot be ignored. The first case is most familiar since the conventional theory of linear sweep voltammetry is applicable. The treatment of finite electrode kinetics for this regime, especially the extraction of standard electrochemical rate constants,  $k_s$ , from cyclic voltammetry, is well known [8]. However, consideration of the combined effects of solution resistance,  $R_s$ , and finite electrode kinetics, necessary for the extraction of reliable rapid rate parameters, is relatively rare, even in this case [1,5]. Some model calculations demonstrate the importance of  $R_s$  in limiting the evaluation of  $k_s$  for typical microelectrode voltammetric experiments [5]. In the steady-state voltammetric case, separate treatments have appeared for the influence of solution resistance [6,7] or finite electrode kinetics [9].

The intermediate scan rate regime, although more complex, is nonetheless of substantial practical importance. This case, involving radial diffusion under non-steady-state conditions, has been treated in the absence of complications from finite kinetics and solution resistance [10]. Earlier, Heinze presented digital simulation

results which include the effects of finite kinetics [11], although solution resistance was not considered.

The present communication outlines results from a digital simulation study of cyclic voltammetry at a microdisk electrode, which accounts for the effect of both finite kinetics and solution resistance within the radial as well as linear diffusion regimes. A primary objective is to ascertain the degree to which the extraction of  $k$ , values from microelectrode cyclic voltammetry can be influenced by the combined effects of radial diffusion and solution resistance. The findings here are given in the form of specific examples to lend reality to the discussion; more detailed results will follow in a subsequent publication.

## RESULTS AND DISCUSSION

The specific conditions chosen for the present simulations involve a  $5\text{ }\mu\text{m}$  radius disk at applied potential scan rates,  $v$ , between  $5$  and  $1000\text{ V s}^{-1}$ , with solution resistances,  $R_s$ , between  $0$  and  $2 \times 10^6\text{ }\Omega$ . The latter range was selected since it corresponds to solution conditions that are commonly encountered\*. The reaction is presumed to involve one-electron transfer, with the transfer coefficient,  $\alpha$ , equal to  $0.5$ , and the diffusion coefficients for both the oxidized and reduced forms,  $D_{ox}$  and  $D_{red}$ , being set at  $1.0 \times 10^{-5}\text{ cm}^2\text{ s}^{-1}$ . The simulations refer to cathodic-anodic voltammograms at  $25^\circ\text{C}$ . for  $1\text{ M}$  solution concentration of the oxidized form and in the absence of the reduced form. Since an efficient means of accounting for two-dimensional mass transport is required, the method of simulation chosen was the explicit "fast" Hopscotch algorithm [14] implemented in cylindrical coordinates with an exponentially expanding grid in both dimensions. Results for non-zero  $R_s$  values were achieved by an iterative process (cf. ref. 1). Programs were written in FORTRAN 77. Short time-scale simulations were generated on a Zenith 80386-based microcomputer using 64-bit precision. More demanding calculations employed the Purdue University Cyber 205 supercomputer, again with 64-bit precision.

Figure 1 shows representative plots of the cathodic-anodic peak potential separation,  $\Delta E_p$ , versus  $v^{-1/2}$  for standard electrochemical rate constants,  $k_s$ , from  $0.1$  to  $2\text{ cm s}^{-1}$  as well as the reversible case ( $k_s \rightarrow \infty$ ). (See figure caption for details.) The results for the reversible case (asterisks) agree well with those of Heinze [11],  $\Delta E_p$  increasing systematically with decreasing  $v$ . At suitably high scan rates ( $\geq 10^3\text{ V s}^{-1}$ )  $\Delta E_p$  for the reversible curve approaches  $57\text{ mV}$ , thereby mimicking the behavior of a conventional (infinite plane) electrode [15]. The other  $\Delta E_p - v^{-1/2}$  traces show noticeable deviations from the reversible curve, even for rate constants as large as  $1\text{ cm s}^{-1}$ . The asymptotic tail of these curves at low scan rates is

\* Thus, for example, the specific resistivity,  $\rho$ , for tetrahydrofuran and for dichloromethane, both containing  $0.1\text{ M}$  tetrabutylammonium perchlorate, is  $2670$  and  $725\text{ }\Omega\text{ cm}$ , respectively [12]. Given that [13]  $R_s = \rho/4r_0$ , for a  $5\text{ }\mu\text{m}$  radius electrode we calculate  $R_s$  values of  $1.35 \times 10^6$  and  $3.6 \times 10^5\text{ }\Omega$  in these two media.

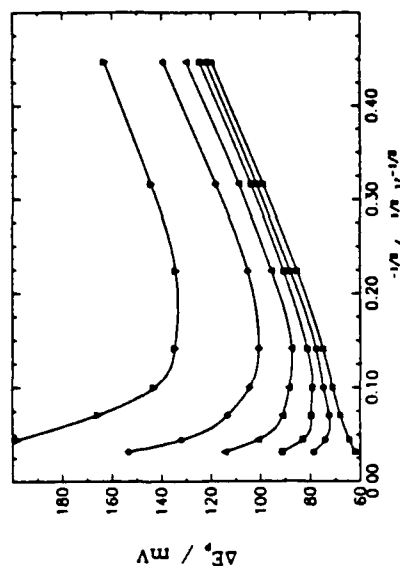


Fig. 1. Plots of simulated cathodic-anodic peak separation,  $\Delta E_p$ , versus the reciprocal square root of the potential scan rate,  $v^{-1/2}$ , at a  $5\text{ }\mu\text{m}$  radius disk electrode for a range of standard rate constants  $k_s$ : (•)  $\rightarrow \infty$ ; (■)  $2.0$ ; (▲)  $1.0$ ; (♦)  $0.5$ ; (▼)  $0.25$ ; (☆)  $0.1$ ; (◊)  $0.05$ . See text for other details.

displaced significantly from the reversible case, suggesting that such voltammetric conditions may contain sufficient kinetic information to provide a useful tool. This observation is intuitively reasonable since mass transport becomes more efficient at lower scan rates as a consequence of radial diffusion; the amount of kinetic information is expected to increase commensurately.

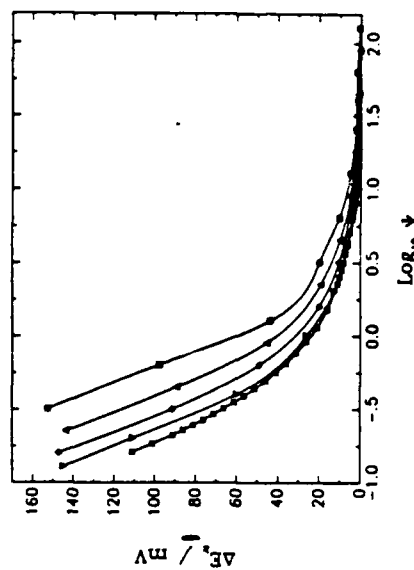


Fig. 2. Plots of peak separation component due to finite electrode kinetics,  $\Delta E_k$ , versus the logarithm of the kinetic parameter  $\psi$  at a  $5\text{ }\mu\text{m}$  radius disk for a range of potential scan rates (•) planar diffusion (see text); (■)  $\infty$ ; (♦)  $50$ ; (▲)  $20$ ; (♦)  $10$ ; (▼)  $5$ ; (☆)  $1$ . See text for other details.

Figure 2 is a more quantitative illustration of the extent to which the enhanced mass transport arising from radial diffusion can convey more kinetic information than the semi-infinite linear case for otherwise similar conditions. Plotted on the y-axis is the "kinetically-induced peak separation",  $\Delta E_k$ , i.e. the additional peak separation due to finite electrode kinetics, as expressed by

$$\Delta E_k = \Delta E_p - \Delta E_{rev} \quad (1)$$

where  $\Delta E_p$  is the observed peak separation and  $\Delta E_{rev}$  is the reversible value, obtained when  $k_s$  approaches infinity. Plotted on the x-axis is the logarithm of the dimensionless kinetic parameter, expressed as [8]:

$$\psi = (D_{ox}/D_{red})^{1/2} k_s (D_{ox} v F / RT)^{-1/2} \quad (2)$$

The asterisked curve in Fig. 2 is obtained for the conventional case of linear diffusion [8], as encountered for high scan rates and/or relatively large radius disk electrodes. The other traces each refer to a 5  $\mu$ m diameter disk for four sweep rates. In contrast to the linear diffusion case, where a single  $\Delta E_k$ -log  $\psi$  curve applies for all scan rates, for the microelectrode progressively larger  $\Delta E_k$  values are obtained at a given  $\psi$  value as the scan rate decreases (Fig. 2). This result reflects the increasing importance of radial diffusion as the scan rate is decreased, and points to a severe limitation of the conventional "Nicholson analysis" [8], based on  $\Delta E_k$ -log  $\psi$  curves, to extract  $k_s$  values from microelectrode voltammetric data unless this effect is taken into account.

The simulations presented so far presume that the effect of solution resistance is negligibly small. Typically, however, this "ideal" circumstance turns out strictly not to be the case, at least for a 5  $\mu$ m disk. Figure 3 contains a sequence of  $\Delta E_p$ - $v^{-1/2}$  curves analogous to those in Fig. 1, except that each corresponds to reversible kinetics (i.e.  $k_s \rightarrow \infty$ ) with progressively increasing solution resistances,  $R_s$ . (See the figure caption for details; the asterisked trace is identical to that in Fig. 1, since here  $R_s = 0$ ). For simplicity, the effect of the double-layer capacitance is neglected here; consideration of this factor tends to enhance somewhat the effect of solution resistance upon  $\Delta E_p$ .

Comparison between Figs. 1 and 3 shows that the manner and extent to which solution resistance alone increases  $\Delta E_p$  (in the absence of electronic resistance compensation) can be roughly comparable to that of finite kinetics, at least where  $R_s$  is relatively large. For example, the inverted triangles in Fig. 3 refer to a specific resistance,  $R_s$ , of 10<sup>6</sup>  $\Omega$ , which corresponds to a solvent resistivity of 1960  $\Omega$  cm (characteristic of n-propanol with 0.1 M supporting electrolyte [12]). From Fig. 1, the  $\Delta E_p$ - $v^{-1/2}$  curve for 0.5 cm s<sup>-1</sup> ( $\Delta$ ) is closely comparable. Consequently, an ignorance of solution resistance effects in this case could lead mistakenly to a  $k_s$  value of ca. 0.5 cm s<sup>-1</sup> being assigned to a redox couple for which the actual rate constant is substantially larger. Such effects are well known for conventional electrode systems in the presence of significant uncompensated solution resistance,  $R_{un}$ , where the  $\Delta E_p$ - $v$  dependencies engendered by finite electrode kinetics and non-zero  $R_{un}$  are often very similar, and hence difficult to deconvolute [5,16].

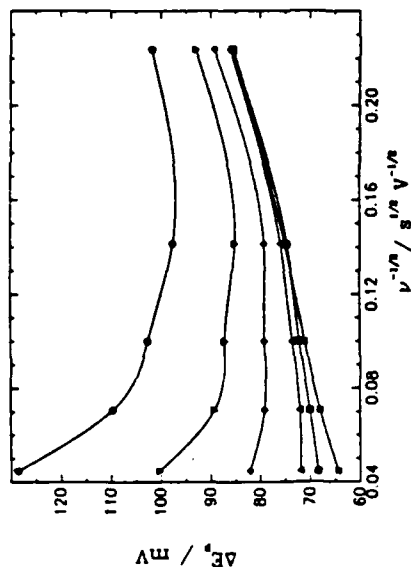


Fig. 3. As for Fig. 1, but for a range of solution resistances,  $R_s$ , with a reversible electrode reaction (i.e.  $k_s \rightarrow \infty$ ).  $R_s$ : (○) 0; (◐)  $1 \times 10^5$ ; (Δ)  $2 \times 10^5$ ; (●)  $5 \times 10^5$ ; (◑)  $1 \times 10^6$ ; (◒)  $2 \times 10^6$ ; (◓)  $5 \times 10^6$ ; (◔)  $1 \times 10^7$ . See text for other details.

Given that the presence of solution resistance may often complicate the extraction of rate data from cyclic voltammograms obtained in the intermediate as well as high scan rate regimes, it is necessary to examine the effects of both factors in concert. In the simplest case, one might anticipate that the two effects will be approximately additive, so that their influence upon  $\Delta E_p$  could be treated independently as in Figs. 1 and 3. Unfortunately, however, there turns out to be a relatively complex interaction between these effects.

This point is illustrated in Fig. 4, which consists of plots of the peak separation component "attributable" to solution resistance effects,  $\Delta E_{res}$ , versus the logarithm of  $R_s$ , obtained for cyclic voltammograms simulated for different  $k_s$  values. The  $\Delta E_{res}$  values were obtained from

$$\Delta E_{res} = \Delta E_p' - \Delta E_k - \Delta E_{rev} \quad (3)$$

where  $\Delta E_p'$  is the total cathodic-anodic peak separation obtained in the presence of both finite kinetics and solution resistance effects, and  $\Delta E_k$  and  $\Delta E_{rev}$  are defined as before. The lower and upper pairs of curves in Fig. 4 correspond to scan rates of 50 and 500 V s<sup>-1</sup>, respectively. The dashed traces refer to  $k_s \rightarrow \infty$ , so that  $\Delta E_k = 0$ ; under these conditions  $\Delta E_{res}$  will simply be the additional peak separation due to the presence of  $R_s$ . The corresponding pairs of solid traces in Fig. 4 refer to  $k_s$  values of 0.5 and 0.1 cm s<sup>-1</sup>, so that  $\Delta E_k > 0$ .

If the effects of solution resistance and finite kinetics are strictly additive, then the solid  $\Delta E_{res}$ -log  $R_s$  traces in Fig. 4 will be coincident with the dashed lines. That this is clearly not the case points to the non-validity of this assertion. The systematically smaller values of  $\Delta E_{res}$  obtained from eqn. (3) in the additional presence of finite kinetics infer that the measured  $\Delta E_p'$  values for systems contain-

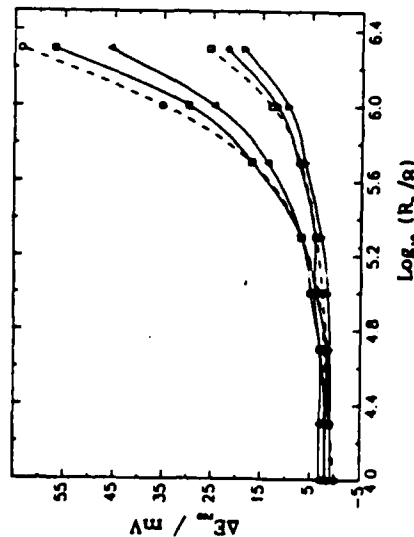


Fig. 4. Plots of resistive contribution to peak separation,  $\Delta E_{w,\infty}$ , obtained from eqn. (3), versus the logarithm of the solution resistance,  $R_s$ , at a  $5 \mu\text{m}$  disk for a range of standard rate constants. Lower and upper three curves correspond to 5 and 50  $\text{V s}^{-1}$  scan rates, respectively. ( $\square$ ,  $\circ$ )  $k_1 \rightarrow \infty$ ; ( $\triangle$ ,  $\square$ )  $k_1 = 0.5 \text{ cm s}^{-1}$ ; ( $\triangle$ ,  $\nabla$ )  $k_1 = 0.1 \text{ cm s}^{-1}$ . See text for other details.

ing both  $R_s$  and  $k_1$  effects will be smaller than anticipated from the influence of these two factors when considered separately. This non-additive nature of solution resistance and electrode kinetic effects has the consequence that  $k_1$  estimates obtained by correcting for the former effect without cognizance of their mutual interaction will be systematically larger than the actual  $k_1$  value; the opposite will be the case if  $R_s$  effects are ignored all together.

Overall, then, it is clearly important to allow for the interactive nature of the effects when extracting  $k_1$  values for microelectrode voltammetric measurements. Unfortunately, proper evaluation of these factors strictly requires an iterative procedure based on digital simulation. A similar iterative procedure is desirable whether or not radial, rather than purely linear, diffusion needs to be taken into account. One relatively straightforward approach for achieving this end is described in ref. 5.

These findings might be construed as presaging the demise of microelectrode voltammetry as a widely applicable strategy for evaluating large  $k_1$  values. This perception is supported by noting that the deleterious influence of uncompensated resistance,  $R_{un}$ , upon  $k_1$  measurements using larger electrodes in the presence of positive-feedback  $R_s$  compensation [5] can be comparable to, or even smaller than, that for microelectrodes in the absence of such electronic compensation. One substantial advantage of microelectrode voltammetry for such purposes, however, is that the value of  $R_{un}$  required for the quantitative extraction of  $k_1$  values is readily amenable to experimental evaluation. In contrast, it is often difficult to determine accurately the  $R_{un}$  value remaining when positive-feedback compensation is employed, limiting the range of  $k_1$  values which can be reliably evaluated under these

conditions [5]. Certainly, the use of smaller microelectrodes than those utilized primarily to date will have considerable advantages in diminishing  $R_s$  effects further, along with enhancing mass transport via radial diffusion.

As a consequence, we suspect that the correction for solution resistance effects when evaluating rapid electrode kinetics can be applied more reliably in the microelectrode case, even though digital simulation techniques may often be necessary in order to provide a complete description of the experimental system. A further, more detailed, analysis of these issues will be provided in a forthcoming report.

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